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Media - What Makes Them Special?

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Chromium Activated Crystals as Tunable Laser Media - What Makes Them Special?*

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1. Abstract

The trivalent chromium ion has been successfully used as the optical activator in a large number of tunable crystalline laser materials. Some of the unique properties of its $3d^3$ electron configuration which have led to this widespread success are reviewed. It is found that a combination of positive attributes has led to a higher probability of success with the use of the Cr^{3+} ion than with other transition metal ions. Some negative factors associated with the use of other transition metal ions are identified as areas in need of attention if they are to be used. Optimization of the performance of chromium doped laser materials under flashlamp pumping is also discussed.

2. Introduction

The use of the Cr^{3+} ion as the optical activator in crystalline laser materials will be discussed in terms of a comparison between Cr^{3+} and other transition metal ions of the same row in the periodic table. It is implicit for some of the arguments made here that the potential for efficient flashlamp pumping of the materials is desirable, although to date this has been achieved in only a few cases. In this context, it is appropriate to begin the discussion with a review of some of the major advantages and difficulties associated with the use of solid state transition metal ion lasers in general.

Because of the parity forbidden nature of transitions within the $3d^n$ configuration of transition metal ions, the excited state radiative life-

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times, τ_r , can be long enough ($\tau_r \geq 100$ ns) to provide for efficient flashlamp pumping with reasonable lamp shot life ($>10^8$ shots). The strong interaction between the electronic energy levels and the crystal vibrations (vibronic interaction) leads to broad absorption and emission bands. This allows for efficient absorption of flashlamp pump light, along with broadly tunable emission. Furthermore, some of the near infrared emission wavelengths are difficult to generate by any other means. The concomitant low emission cross sections reduce the potential for parasitic oscillation and shortening of the excited state lifetime by amplified spontaneous emission (ASE). This will allow energy to be stored in the medium at high density, and increase the achievable output energy per laser aperture.

In addition to possessing good quantum electronic properties, tunable solid state lasers employing transition metal ions as optical activators may also exhibit good physical properties. These include high stability against photo-degradation and high physical durability of the materials. These are significant advantages over many solid state laser materials activated by color centers.

Of course, the above advantages do not come without a price. The broad emission bandwidths create a difficult tradeoff between emission cross section and radiative lifetime which will be discussed in more detail toward the end of this review. If the lifetime is long enough for flashlamp pumping then the emission cross section is low, leading to low gain and high saturation fluences. Low gain implies the necessity to develop low loss material to maintain good output efficiency. High saturation fluences increase the potential for optical damage at pulse intensities required for efficient extraction of the stored energy. Other deleterious effects of the strong vibronic interaction include increased potential for broadband excited state absorption and nonradiative relaxation in many ions.

The development of tunable lasers based on the Cr^{3+} ion began with alexandrite¹, $\text{BeAl}_2\text{O}_4:\text{Cr}$ and was rapidly extended to numerous other crystalline media.² The extraordinary success achieved to date with the Cr^{3+} ion is readily apparent in Table , where all of the currently known tunable solid state laser materials are listed. It is seen that the

number of materials employing Cr^{3+} exceeds the number of materials employing all other transition metals combined. It is worthwhile noting that with the exception of titanium doped sapphire, $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$, virtually all of the materials based on other transition metal ions have only been used at cryogenic temperatures. On the other hand, only one of the Cr^{3+} based materials (ZnWO_4) require cryogenic cooling in order to produce cw laser action. This is largely due to the lower nonradiative relaxation rates exhibited by Cr^{3+} at room temperature.

Table 1. A listing of the (reported) tunable solid state laser materials based on activation by transition metal ions as of June 1986.

Cr^{3+} Lasers	Others
$\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$	$\text{MgF}_2:\text{Ni}^{2+}$
$\text{Be}_3\text{Al}_2(\text{SiO}_3)_6:\text{Cr}^{3+}$	$\text{MnF}_2:\text{Ni}^{2+}$
$\text{Gd}_3(\text{Sc},\text{Ga})_5\text{O}_{12}:\text{Cr}^{3+}$	$\text{MgO}:\text{Ni}^{2+}$
$\text{Gd}_3\text{Sc}_2\text{Al}_3\text{O}_{12}:\text{Cr}^{3+}$	$\text{KMgF}_3:\text{Ni}^{2+}$
$\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Cr}^{3+}$	$\text{CaY}_2\text{Mg}_2\text{Ge}_3\text{O}_{12}:\text{Ni}^{2+}$
$\text{La}_3\text{Lu}_2\text{Ga}_3\text{O}_{12}:\text{Cr}^{3+}$	$\text{MgF}_2:\text{Co}^{2+}$
$\text{Y}_3\text{Ga}_5\text{O}_{12}:\text{Cr}^{3+}$	$\text{ZnF}_2:\text{Co}^{2+}$
$\text{Y}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}:\text{Cr}^{3+}$	$\text{KMgF}_3:\text{Co}^{2+}$
$\text{KZnF}_3:\text{Cr}^{3+}$	$\text{KZnF}_3:\text{Co}^{2+}$
$\text{ZnWO}_4:\text{Cr}^{3+}$	$\text{MgF}_2:\text{V}^{2+}$
$\text{SrAlF}_5:\text{Cr}^{3+}$	$\text{CsCaF}_3:\text{V}^{2+}$
$\text{Na}_3\text{Ga}_2\text{Li}_3\text{F}_{12}:\text{Cr}^{3+}$	$\text{Al}_2\text{O}_3:\text{Ti}^{3+}$
$\text{ScBO}_3:\text{Cr}^{3+}$	

Because the strength of the crystal field has a large effect on the positions of the energy levels, the observed tuning ranges of the various Cr^{3+} doped crystals extends continuously from about 700 nm to nearly 1100 nm. Figure 1 depicts the tuning ranges of representative materials based on Cr^{3+} which have been demonstrated to date.

The broadly successful use of the Cr^{3+} ion is not due to a single factor, but can be attributed to a fortuitous combination of several unique properties of the ion's $3d^3$ electron configuration. These include:

1. The presence of three spin allowed pump bands which allows efficient flashlamp pumping.

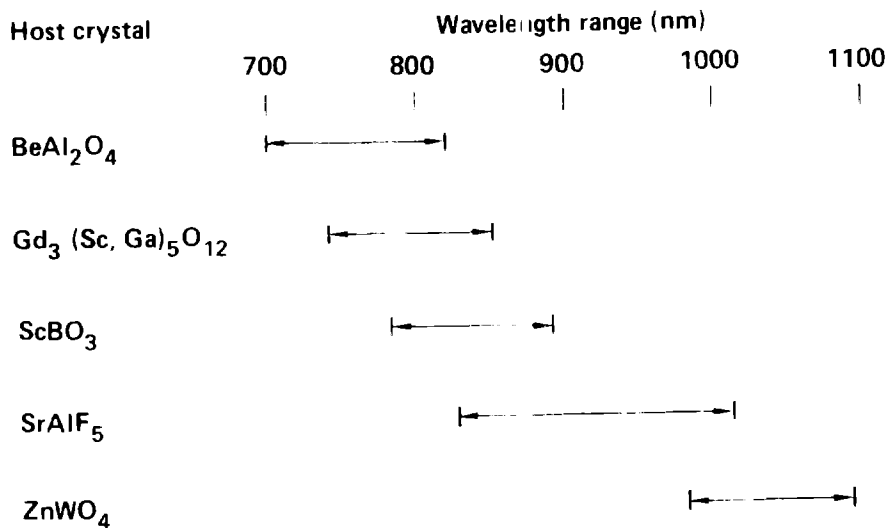


Figure 1. Reported laser tuning ranges for Cr³⁺ ions in representative crystals.

2. Chemical stability--Cr³⁺ is resistant to both oxidation and reduction.
3. The possibility of simultaneous occupation of crystallographic sites with different anion coordination numbers (leading to undesirable spectral characteristics) is minimized by a high octahedral crystal field stabilization energy (CFSE). This is especially important in crystals with both octahedral and tetrahedral cation sites (e.g. garnets).
4. Electron pairing does not produce a low-spin first excited state up to relatively high crystal field strengths, so the dominant emission is usually spin allowed.
5. The relatively large crystal field splittings available stabilize the first excited state against nonradiative relaxation.
6. The positions of the second and third spin allowed absorption bands result in a gap in the excited state absorption spectrum at the emission wavelengths.

These points will be discussed in more detail in the following section.

3. Discussion of the Special Attributes of Trivalent Chromium

3.1 Pump Bands

If flashlamp pumping is to be employed, then it is important to have broad absorption bands above the metastable state to obtain high lasing efficiency. The strongest absorption bands will be ones for which the spin quantum number does not change (i.e. spin allowed transitions). The spin allowed absorption bands of the various $3d^n$ electron configurations are enumerated in Table 2. It is seen the Cr^{3+} ion with three spin allowed pump bands is one of a group of ions with the maximum number. In Fig. 2, for example, it is seen that the absorption bands of $\text{SrAlF}_5:\text{Cr}$ span the entire range of visible and near ultraviolet wavelengths.

Table 2. An enumeration of the spin allowed absorption (pump) bands for the common transition metal ions.

<u>Ion(s)</u>	<u>Configuration</u>	<u>Spin allowed pump bands</u>	<u>Total</u>
$\text{Ti}^{3+}, \text{V}^{4+}$	$3d^1$	${}^2E(g)$	1
$\text{Ti}^{2+}, \text{V}^{3+}$	$3d^2$	${}^3T_2(t_2e), {}^3T_1(t_2e), {}^3A_2(e^2)$	3
$\text{V}^{2+}, \text{Cr}^{3+}, \text{Mn}^{4+}$	$3d^3$	${}^4T_2(t_2^2e), {}^4T_1(t_2^2e), {}^4A_1(t_2e^2)$	3
$\text{Cr}^{2+}, \text{Mn}^{3+}$	$3d^4$	${}^5T_2(t_2^2e^2)$	1
$\text{Mn}^{2+}, \text{Fe}^{3+}$	$3d^5$	-	0
$\text{Fe}^{2+}, \text{Co}^{3+}$	$3d^6$	${}^5E(g, e^3)$	1
Co^{2+}	$3d^7$	${}^4T_2(t_2^4e^3), {}^4T_1(t_2^4e^3), {}^4A_2(t_2^3e^4)$	3
Ni^{2+}	$3d^8$	${}^3T_2(t_2^5e^3), {}^3T_1(t_2^5e^3), {}^3A_1(t_2^4e^4)$	3
Cu^{2+}	$3d^9$	${}^2T_2(t_2^5e^4)$	1

Comparing Tables 1 and 2 it can be seen that Ti^{3+} is the only ion with fewer spin allowed pump bands that has been employed as a laser crystal activator. It should be noted however that the absorption band of $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$ (titanium-sapphire) is quite broad due to strong Jahn-Teller splitting of the 2E level, which improves its absorption efficiency considerably.

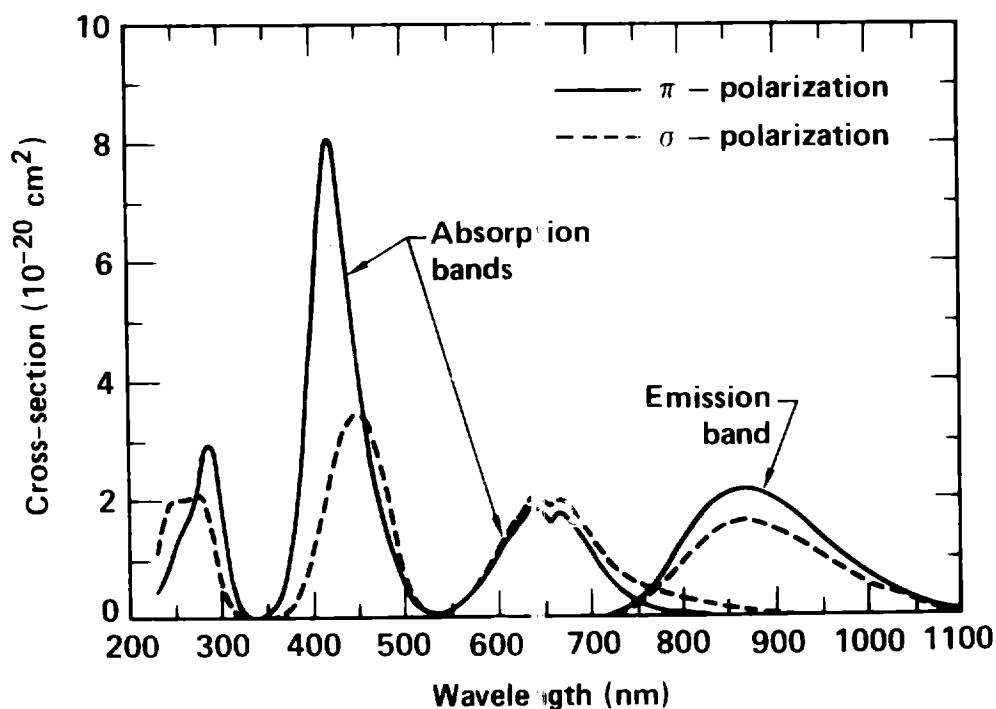


Figure 2. The absorption spectra of $\text{Sr/1F}_5\text{:Cr}$ showing three bands spanning the visible and near ultraviolet wavelengths.

3.2 Chemical Stability

In many instances it is possible for transition metals to enter crystal lattices in more than one valence state. The problem can be especially difficult if the desired valence state is different from that of the natural site in the host crystal. The Cr^{3+} ion has been used to produce laser emission in KZnF_3 and ZnWO_4 , where it substitutes for the divalent Zn^{2+} ion. Such behavior has not been demonstrated in any other transition metal ion to date.

In some cases alternate valence states create problems associated with the production of undesirable absorption bands. In other cases it simply reduces the number density of the desired ionic species. Ti^{3+} , for example, is readily oxidized to Ti^{4+} , thus reducing the available concentration of the desired lasing species. Special measures must be taken (e.g. heat treatment in a reducing environment) to stabilize the Ti^{3+} valence state.

Table 3. A comparison of the relative stability against chemical oxidation and reduction for common transition metal ions.

<u>Ion</u>	<u>Configuration</u>	<u>Stability against oxidation</u>	<u>Stability against reduction</u>
Ti ³⁺	3d ¹	Low	High
V ⁴⁺	3d ¹	Moderate	Low
Ti ²⁺	3d ²	Low	High
V ³⁺	3d ²	Moderate	Moderate
V ²⁺	3d ³	Low	High
Cr ³⁺	3d ³	High	High
Mn ⁴⁺	3d ³	High	Low
Cr ²⁺	3d ⁴	Low	High
Mn ³⁺	3d ⁴	Moderate	Low
Mn ²⁺	3d ⁵	High	High
Fe ³⁺	3d ⁵	High	Low
Fe ²⁺	3d ⁶	High	High
Co ³⁺	3d ⁶	High	Low
Co ²⁺	3d ⁷	High	High
Ni ²⁺	3d ⁸	High	Moderate
Cu ²⁺	3d ⁹	High	Low

The relative stability of the various common transition metal ions against oxidation and reduction is shown in Table 3. Ions not appearing in Table 3 are uncommon because their valence is particularly difficult to achieve. The relative stabilities against oxidation and reduction for the various ions were determined by examining the standard reduction potentials of the electrochemical series.³ It is seen that Cr³⁺ is one of only four ions that is resistant to both oxidation and reduction.

3.3 Stability in Octahedral Coordination

In crystals, transition metal cations are most often bonded to four (tetrahedral) or six (octahedral) neighboring anions. Octahedral anion coordination is important for several reasons. First, octahedral coordination produces significantly higher crystal field splittings (i.e. energy gaps between excited states) than tetrahedral coordination. For equal anion charges and metal-ligand distances, for example, the ratio of the tetrahedral to octahedral crystal field strength is given by⁴

$$Dq(\text{tet})/Dq(\text{oct}) = 4/9 \quad (1)$$

Higher crystal field splitting generally results in a greater stability of the metastable excited states against nonradiative relaxation.

Secondly, octahedral coordination generally induces much smaller transition oscillator strengths between states of the $3d^n$ configurations. This is because these ion sites often exhibit inversion symmetry (or near inversion symmetry). Tetrahedral sites, on the other hand, lack inversion symmetry in the extreme, leading to greater mixing of electronic configurations with opposite parity, and consequently produce much higher transition oscillator strengths. High oscillator strengths lead to short radiative lifetimes for the metastable states and therefore make storage of flashlamp pump energy more difficult. In octahedral coordination radiative lifetimes greater than 100 μ s are common.

There are numerous crystals which possess both octahedral and tetrahedral cation sites. Moreover, it is not unusual for the same ion, or for ions with the same valence to be located on such differing sites. The generic formula for an oxide garnet crystal, for example, is $A_3B_2C_3O_{12}$, where A is an 8-fold coordinated (dodecahedral) site, B is a 6-fold coordinated (octahedral) site, and C is a 4-fold coordinated (tetrahedral) site. In gadolinium gallium garnet (GGG), $Gd_3Ga_5O_{12}$, the gallium ions reside on both the octahedral and tetrahedral sites. In gadolinium scandium gallium garnet (GSGG), most of the octahedral sites are occupied by scandium ions which have the same +3 valence as gallium.

As a dopant in garnet crystals Cr^{3+} occupies only the octahedral sites. If there were Cr^{3+} ions on the tetrahedral sites an absorption band would appear at longer wavelength than the normal Cr^{3+} bands due to the reduced crystal field strength at these sites. Such longer wavelength absorption would most likely overlap the Stokes shifted emission band of the normal octahedrally coordinated Cr^{3+} ions. Furthermore the intensity of this absorption would be high due to the lack of inversion symmetry. Laser action would therefore be inhibited or quite possibly prevented altogether by the increased losses at the normal laser wavelengths. Thus, if Cr^{3+} had even a slight tendency to occupy tetrahedral sites, it is very likely that none of the six oxide garnets in Table 1 would exhibit laser action. (It should be noted that tetrahedrally coordinated Cr^{3+} has been reported in $LiAlO_4$.)⁵

The strong preference of Cr^{3+} for octahedral coordination can be understood qualitatively through the model depicted in Fig. 3. In octahedral coordination the d-orbitals which are 5-fold degenerate in the free ion split into low-energy, triply-degenerate t_{2g} orbitals, and high energy, doubly-degenerate e_g orbitals. The magnitude of the splitting is (by definition) $10Dq(\text{oct})$. Relative to the center of gravity of the configuration, then, the t_{2g} levels lie at $-4Dq(\text{oct})$, and the e_g levels lie at $+6Dq(\text{oct})$. The lowest energy state for the $3d^3$ electrons of the Cr^{3+} ion is obtained with one electron in each of the t_{2g} orbitals with parallel spins. The crystal field stabilization energy (CFSE) of this configuration would therefore be $-4Dq(\text{oct}) \times 3 \text{ electrons} = -12Dq(\text{oct})$ relative to the center of gravity.

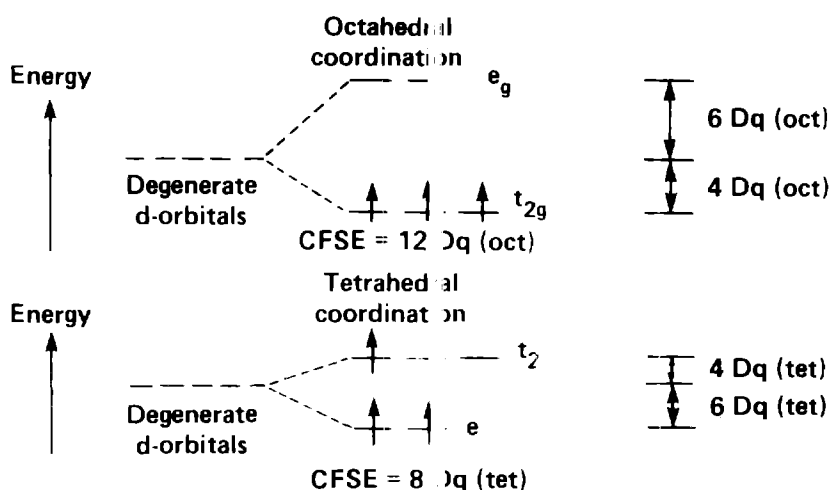


Figure 3. The model used to describe the high octahedral crystal field stabilization energy (CFSE) of the Cr^{3+} ion.

For a tetrahedral site, on the other hand, the e -orbitals lie below the t_2 orbitals. In order to avoid spin pairing (and consequent electrostatic repulsion energy), therefore one of the $3d^3$ electrons must reside in an upper t_2 orbital. The CFSE of this configuration is $-6Dq(\text{tet}) \times 2 \text{ electrons} + 4Dq(\text{tet}) \times 1 \text{ electron} = -8Dq(\text{tet})$. Taking Eq. 1 into account, therefore, the net excess stabilization energy for octahedral coordination over tetrahedral coordination of Cr^{3+} is approximately $-8.5Dq(\text{oct})$. For typical crystals this amounts to an energy of about 1 eV, which is a substantial fraction of the binding energy per cation.

By a similar process it can readily be seen that no other $3d^n$ configuration can have an excess CFSE higher than Cr^{3+} . Data for a number of ions is given in Table 4.⁶ It is seen that Cr^{3+} has by far the highest excess CFSE of any of the transition metal ions listed. The high spin state of the $3d^5$ configuration has no net preference at all for octahedral coordination because one electron resides in each of the 5 orbitals in either coordination. It is interesting to note, for example, that magnetite, Fe_3O_4 , is an inverse spinel, where the Fe^{3+} ions occupy both octahedral and tetrahedral sites, while the Fe^{2+} ion resides on the other octahedral site.⁷ It should be noted that the low CFSE of Ti^{3+} should not be a problem in crystals without tetrahedral sites, such as Al_2O_3 .

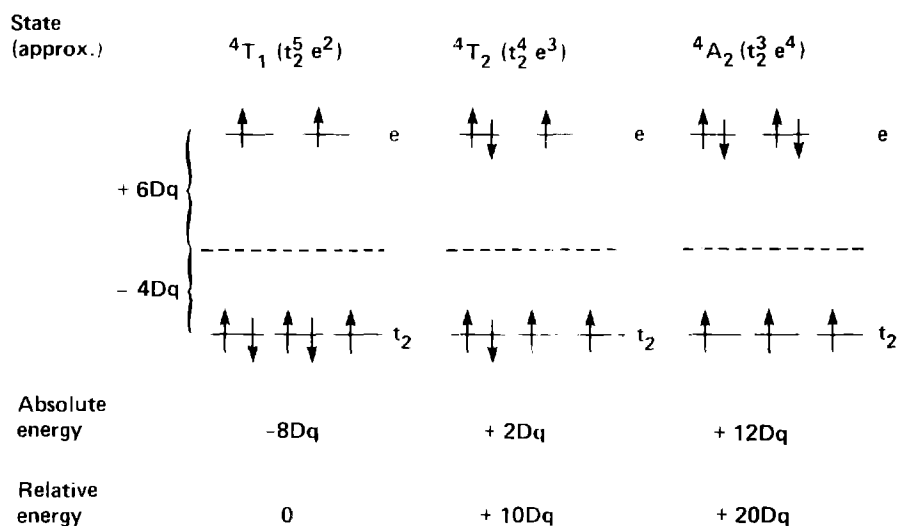
Table 4. Crystal field stabilization energies (kJ mol^{-1}) estimated for transition metal oxides.⁶

Ion		Octahedral stabilization	Tetrahedral stabilization	Excess octahedral stabilization
Ti^{3+}	d1	87.6	58.7	28.9
V^{3+}	d2	160.5	106.8	53.6
Cr^{3+}	d3	225.0	67.0	158.0
Mn^{3+}	d4	135.8	40.2	95.5
Fe^{3+}	d5	0	0	0
Mn^{2+}	d5	0	0	0
Fe^{2+}	d6	49.9	33.1	16.8
Co^{2+}	d7	93.0	62.0	31.0
Ni^{2+}	d8	122.3	36.0	86.3
Cu^{2+}	d9	90.5	26.8	63.7

3.4 Absence of Low Spin First Excited States in Moderate Crystal Fields

There are a number of transition metal ions which can exhibit low spin first excited states in only moderate strength crystal fields. Once the crystal field exceeds a certain critical value, then, the downward fluorescence transition becomes spin forbidden, with a significant reduction in emission oscillator strength. Thus, in order to maintain a reasonably high cross section for stimulated emission, the crystal field strength must be kept below this critical value. Unfortunately, this leads to considerably longer wavelength emission and, in general, less stability against nonradiative relaxation. A case in point is the Co^{2+} ion which has been shown to exhibit laser emission in a number of low crystal field host materials, but only at cryogenic temperatures where nonradiative relaxation is minimized.

Low energy high spin states



Lowest energy low spin state

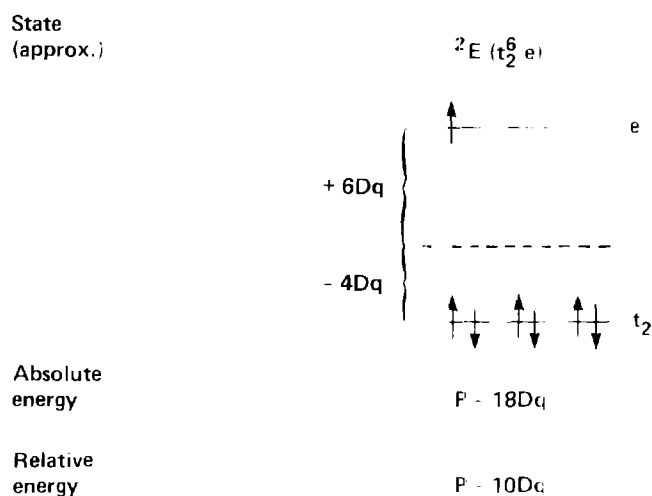


Figure 4. The low energy high spin states and the lowest energy low spin state of Co^{2+} , and the approximate dependence of their energy on the strength of the crystal field.

The conditions which produce low spin first excited states in moderate crystal fields can be understood qualitatively by considering the $3d^7$ configuration of the Co^{2+} ion as depicted in Fig. 4. At low crystal

fields (i.e. small Dq) the lowest energy levels are high spin states. The lowest energy low spin state is also shown in the figure. For very small crystal fields, the energy of this low spin state is higher than that of the high spin states due to the additional electrostatic repulsion energy of the third pair of electrons filling the t_{2g} orbitals. As the crystal field increases, the energy of the low spin state decreases relative to the ground state because of the additional electron in the t_{2g} orbital.

Let P represent the additional "spin pairing" energy of the low spin ${}^2E(t^6_e)$ state. The energy separation between the ${}^2E(t^6_e)$ and ${}^4T_2(t^4_e t^3_g)$ levels is $P - 20Dq$ as shown in Fig. 4. For small crystal fields ($10Dq < P/2$), the first excited state is ${}^4T_2(t^4_e t^3_g)$. For crystal fields in the intermediate range, $P/2 < 10Dq < P$, the first excited state becomes the low spin ${}^2E(t^6_e)$ state. For high crystal fields, $10Dq > P$, the low spin state would actually become the ground state, but the transition between the first excited state and the ground state would still remain spin forbidden. Thus, only for crystal field strengths less than the critical value, $10Dq = P/2$, is the transition between the first excited state and the ground state spin allowed and of reasonably high oscillator strength. The $3d^4$, $3d^5$, $3d^6$, and $3d^7$ configurations all exhibit similar behavior as can be seen in their Tanabe-Sugano diagrams⁸ in Fig. 5.

3.5 Availability of Higher Crystal Field Splittings

In contrast to the situation described above, trivalent chromium does not exhibit a low spin first excited state until moderately high crystal fields are reached. Tunable laser emission has been observed on the spin allowed 4T_2 to 4A_2 transition at much shorter, near infrared wavelengths. The effects of nonradiative relaxation in Cr^{3+} are reduced, and room temperature operation can usually be attained.

Arguments completely analogous to that given above show that the first excited state of the $3d^3$ configuration of Cr^{3+} does not drop in energy relative to the ground state. Thus, the crystal field strength at which the first excited state becomes a low spin state is approximately doubled (i.e. the critical field strength is now given by $10Dq \sim P$), as is clearly seen in Fig. 6. At higher crystal fields Cr^{3+} exhibits the

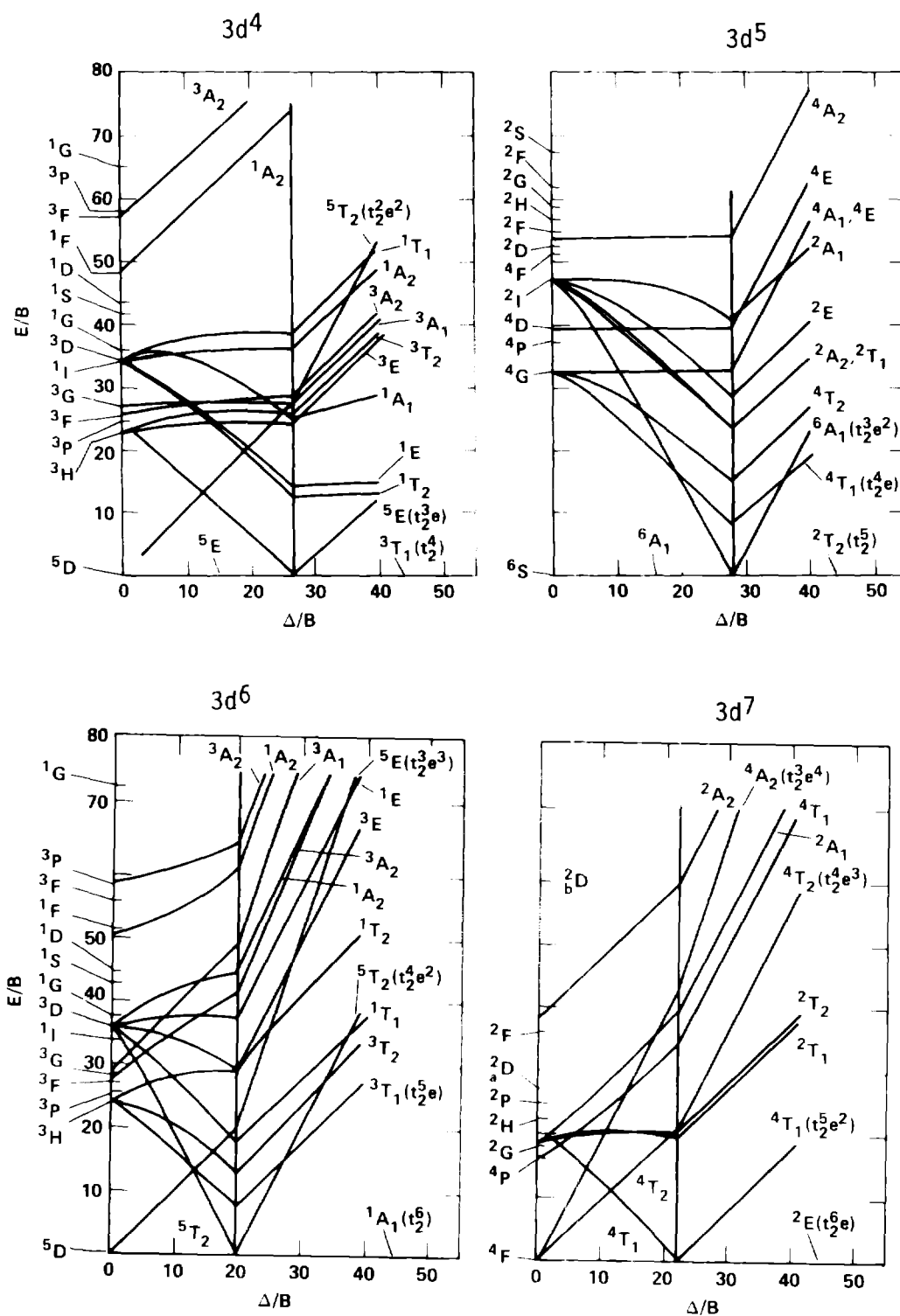


Figure 5. The Tanabe-Sugano diagrams for the $3d^4$, $3d^5$, $3d^6$, and $3d^7$ configurations showing low spin states which drop in energy as the crystal field increases.⁸

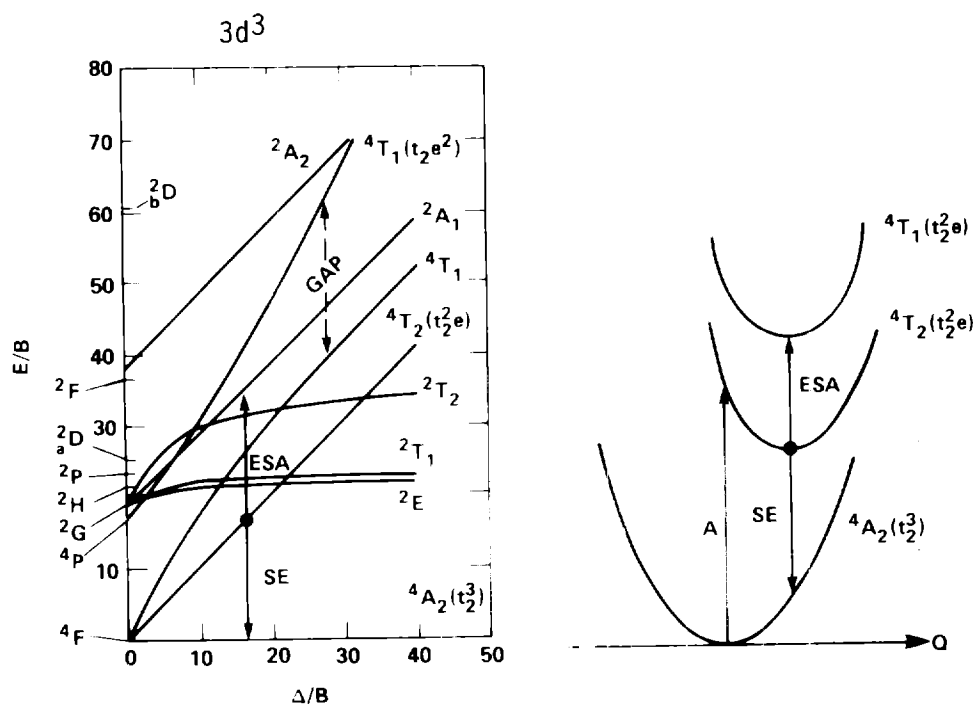


Figure 6. The Tanabe-Sugano diagram for the $3d^3$ configuration shows that the low spin states do not drop in energy as the crystal field increases. Excited state absorption from the $4T_2$ level falls in the gap between the second and third states of the same spin. The diagram on the right indicates that the ESA to the first $4T_1$ excited state should be narrow (with a small Stokes shift) because it has the same number of e-electrons as the $4T_2$ state.

familiar spin-forbidden, R-line emission, which is responsible for 3-level narrowband laser action in ruby. It should be noted that the spin forbidden transitions in the $3d^4$, $3d^5$, $3d^6$, and $3d^7$ configurations would be broad rather than narrowband, thus leading to much smaller cross sections for stimulated emission at any given wavelength.

Examination of the Tanabe-Sugano diagrams for the $3d^2$ and $3d^8$ configurations show that they exhibit behavior similar to trivalent chromium in this regard. Furthermore, the $3d^1$ and $3d^9$ configurations are even better because for these simple "one-electron" configurations there is no possibility of spin pairing, and therefore there is only one state of the spin. All of these configurations should exhibit generally higher resistance to nonradiative relaxation in the higher crystal field environments.

3.6 Reduced Excited State Absorption

To date there is very little in the way of direct measurements of the effects excited state absorption (ESA). However, in most of the $3d^n$ ions ($2 < n < 8$) there are a large number of energy levels which produce such absorption (upward transitions) from the metastable upper laser level. These reduce the available gain and efficiency of any laser based on these ions and, if strong enough can inhibit laser action altogether. Note that for $n = 1$, and $n = 9$, this is not a problem since there is only one excited state of the configuration (neglecting minor splittings).

Upward transitions which are spin allowed are generally the strongest, and therefore are of most concern. For the $3d^3$ configuration of Cr^{3+} ESA is reduced because upward transitions at the laser emission wavelength fall in a gap between the two higher lying states of the same spin as illustrated in Fig. 6. Furthermore, since the first and second excited states have the same number of e_g electrons, there should be less of a shift in the position of the configuration coordinate potential energy minimum. Thus, the lower energy ESA band should be narrow, with less chance of overlapping the emission band. However, mixing of the two 4T_1 bands will broaden this absorption, especially at lower crystal field strengths. Measurements of excited state absorption in Cr^{3+} by Andrews, et.al.⁹ confirm that the emission band falls between the two spin allowed ESA bands, but the lower ESA band was found to be much broader than expected in GSGG:Cr. Because the excited state absorption is nonvanishing in the region between the two 4T_1 ESA bands, it is still of significant concern for Cr^{3+} lasers.

It is also important to point out that excited state absorption bands will not have a significant effect if they are sufficiently weak. This is apparently the case for $MgF_2:Co^{2+}$ ($3d^7$) which exhibits very high lasing efficiency at cryogenic temperatures.¹⁰

4. Summary Comparison of $3d^n$ Ion Properties

An overall scorecard comparing the properties of the various common 3d transition metal ions in light of the foregoing discussions is displayed in Table 5. The qualitative grades given in the table are generally self explanatory. Question marks (?) indicate some uncertainty, ambiguity or

unavailability of data. It is clear from the overall ratings that the $3d^3$ configuration of the Cr^{3+} ion has the highest probability for successful usage. The ion exhibits a number of positive attributes, so the discovery of a large number of tunable lasers based on it is understandable.

However, it could also be said that the success to date with Cr^{3+} is to some extent simply a result of improved statistics. Table 5 is also good for pointing out areas of special concern if other ions are to be used successfully. If an adequate job of valence stabilization is done, and if tetrahedral coordination can be avoided (as in Al_2O_3) then the Ti^{3+} ion looks very attractive. Similarly, if chemically stable conditions can be attained, the Mn^{4+} and Cu^{+} ions also look interesting. On the other hand there is clearly not much you can do with Fe^{3+} .

Table 5. An overall comparison (scorecard) of the attributes of the common transition metal ions discussed in Section 3.

Configuration	Ion	No. of pump bands	Chemical stability	Octahedral stabilization	Absence of low spin first excited states	Large crystal field splitting	Reduced ESA
$3d^1$	Ti^{3+}	1	—	—	++	++	++
$3d^1$	V^{4+}	1	—	—	++	++	++
$3d^2$	Ti^{2+}	3	—	+	+	+	—
$3d^2$	V^{3+}	3	?	+	+	+	—
$3d^3$	V^{2+}	3	—	++	+	—	?
$3d^3$	Cr^{3+}	3	+	++	+	+	+
$3d^3$	Mn^{4+}	3	—	++	+	+	+
$3d^4$	Cr^{2+}	1	—	++	—	—	+
$3d^4$	Mn^{3+}	1	—	++	—	—	+
$3d^5$	Mn^{2+}	0	+	—	—	—	—
$3d^5$	Fe^{3+}	0	—	—	—	—	—
$3d^6$	Fe^{2+}	1	+	—	—	—	+
$3d^6$	Co^{3+}	1	—	—	—	—	+
$3d^7$	Co^{2+}	3	+	+	—	—	?
$3d^8$	Ni^{2+}	3	+	+	+	?	?
$3d^9$	Cu^{2+}	1	—	+	++	?	++

5. The Tradeoff Between Emission Cross Section and Excited State Lifetime

For flashlamp pumped energy-storage lasers it is desirable to have the excited state lifetime as long as possible consistent with a reasonably high cross section for stimulated emission. Short lifetimes require short flashlamp pulsewidths to produce efficient operation, resulting in reduced shot life of the lamps. Low emission cross sections imply high saturation fluences. If the saturation fluence is too high the material can undergo optical damage at fluences required for efficient energy extraction. As a rough guideline lifetimes greater than about 100 μs , and emission cross sections greater than $2 \times 10^{-20} \text{ cm}^2$ are desirable.

Unfortunately, in an isotropic material the product of the peak emission cross section, σ_L , and radiative lifetime, τ_r , are constrained by the relation

$$\sigma_L \tau_r = \frac{\lambda_L^2}{8\pi c n^2 \Delta\nu} \quad (2)$$

where λ_L is the peak emission wavelength, n is the refractive index of the material, and $\Delta\nu$ is the effective bandwidth of the fluorescence emission. This relation is plotted in Fig. 7 for values of $\lambda_L = 750 \text{ nm}$, and $\Delta\nu = 1700 \text{ cm}^{-1}$ which are typical of Cr^{3+} emission.¹¹ The solid curves in the figure are for $n = 1.44$ (typical of fluoride materials) and $n = 1.85$ (typical of oxide materials). Also plotted are lifetimes and cross sections estimated on the basis of spectroscopic measurements of chromium emission in a number of hosts. It can be seen that it is quite difficult to achieve an acceptable tradeoff in an isotropic material.

It has been recognized by a number of researchers, although perhaps not widely appreciated, that the tradeoff can improve considerably in anisotropic media. In a uniaxial crystal, for example, the emission cross sections, σ_π and σ_σ , for π - and σ -polarizations, respectively, can be treated independently according to

$$\sigma_\pi = \frac{\lambda_L^2}{8\pi c n^2 \Delta\nu} A_\pi \quad (3)$$

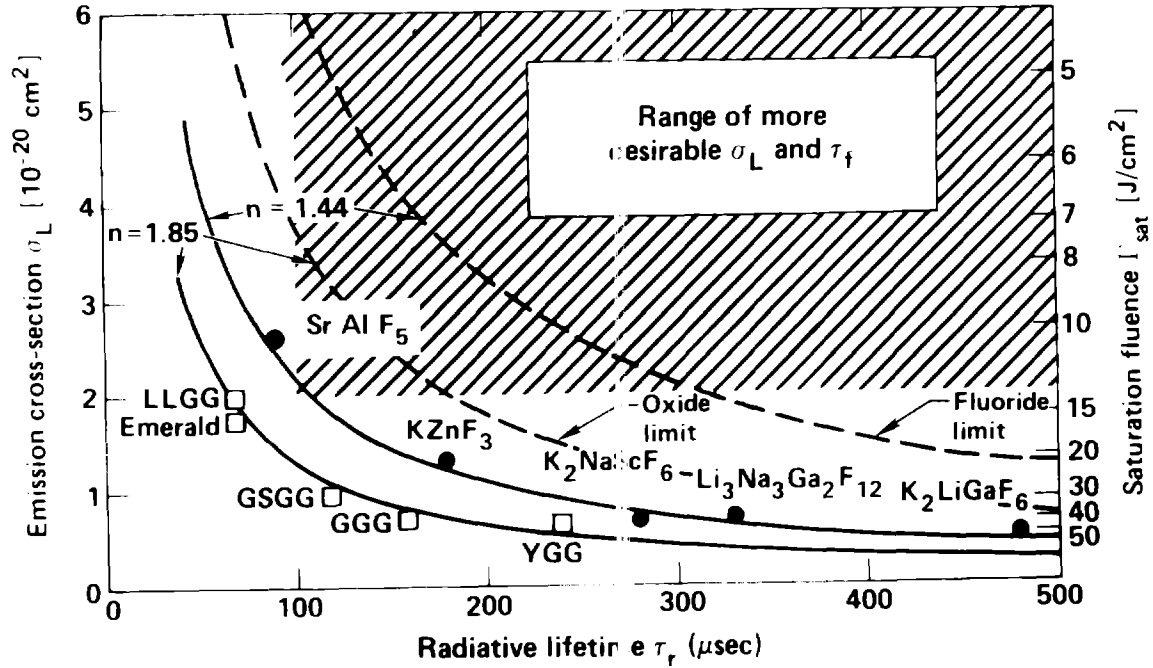


Figure 7. Illustrating the difficult tradeoff between radiative lifetime and emission cross section. Curves were generated using Eqs. (2) and (6) with $\lambda_L = 750 \text{ nm}$, $\Delta\nu = 1700 \text{ cm}^{-1}$, and $n = 1.85$ (typical of oxides) or $n = 1.44$ (typical of fluorides). Solid curves are for isotropic media while dashed curves are for idealized anisotropic media with emission concentrated in one polarization.

and,

$$\sigma_\sigma = \frac{\lambda_L^2}{8\pi cn^2 \Delta\nu} A_\sigma \quad (4)$$

where A_π and A_σ are the spontaneous emission rates for the two polarizations. The total radiative decay rate is given by

$$\frac{1}{\tau_r} = \frac{1}{3} A_\pi + \frac{2}{3} A_\sigma \quad (5)$$

The optimum situation occurs when the emission rate for π -polarization is substantially higher than that for σ -polarization. If the σ -polarized emission rate can be neglected (3) and (5) can be combined to yield

$$\sigma_{\pi} \tau_r \approx 3 \cdot \frac{\lambda_L^2}{8\pi c n^2 \Delta\nu} \quad (6)$$

Thus, as much as a factor of three increase in the σ - τ product can be had if the emission dipoles are appropriately aligned. The dashed curves in Fig. 7 were obtained by multiplying the solid curve values by 3, thereby indicating the approximate limiting values which can be achieved in highly anisotropic media.

It is well known that the biaxial crystal alexandrite, $\text{BeAl}_2\text{O}_4:\text{Cr}$, exhibits just such a high anisotropy, with the emission rate in one polarization exceeding that of each of the other two by a factor of 10.¹ However, the advantage is substantially reduced in this case by the sharing of population between the ^2E and $^4\text{T}_2$ levels which lowers the effective emission cross section.

6. Conclusion

The Cr^{3+} ion has been used as the optical activator in numerous crystalline laser materials. It has been shown that this success can be attributed to a number of positive attributes of its $3d^3$ electron configuration. While excited state absorption is reduced due to the positions of the spin allowed ESA bands, its nonvanishing effect on laser emission is still of significant concern, and may limit achievable efficiency in many materials. A number of other transition metal ions show promise if their weak points can be overcome. Finally, improvements in performance of flashlamp pumped materials are possible through the alignment of emission dipoles in anisotropic media.

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